A RADIOCHEMICAL DETERMINATION OF CHLORINE EXCHANGE BETWEEN POTASSIUM HEXACHLORORHENATE (IV) AND HYDROCHLORIC ACID

A Thesis

Presented to

The Graduate Division

Drake University

In Partial Fulfillment

of the Requirements for the Degree

Master of Arts

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by

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August 1963

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CHAPTER I

THE PROBLEM AND DEFINITIONS OF TERMS USED

Within the last two decades, the use of radioactive tracer atoms has become a very common and useful tool in analyzing chemical compounds and their various reactions. The technique of "tagging" a reactant and observing its progress and location throughout a reaction has enabled scientists to obtain a more thorough understanding of certain molecular structures and reactions. Many reactions, which had been previously assumed to be relatively simple one-step problems, are now, because of radio-tracer data, understood to be much more complex.

The science of chemistry is still very much in the data collecting stage of its evolution, for there are many elements about which much is still not known. Many chemists are studying little-known compounds, especially of the more rare elements, in an effort to derive further knowledge about these elements.

Considerable research has been done on the chemistry of rhenium since its discovery by the Noddacks in 1925.[1]

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[1] I. Noddack and W. Noddack, Das Rhenium (Leipzig: Voss, Inc., 1933), p. 4.

However, there is still information to be gained, particularly about the nature of the rhenium complex ions.

I. THE PROBLEM

Statement of the problem. The purpose of this experiment is to study the compound potassium hexachlororhenate (K_2ReCl_6) in an exchange reaction as follows: (1) to determine if the reaction

$$Cl^{36-} + ReCl_6^{=} \dashrightarrow ReCl_5Cl^{36=} + Cl^-$$

does or does not occur, and (2) if an exchange does take place due to ionization, then further experimentation could be performed to determine the mechanism of this exchange. In both instances the radioactive tracer technique can be used to make these determinations. Hydrochloric acid, since it is a strong acid--that is it will ionize almost completely in an aqueous solution--can be used as the common ion tracer agent, with chlorine-36 as the tagged atom in the acid.

Justification of the problem. Murmann,[1] in his work with perrhenate, observed that there was an exchange of oxygen atoms between perrhenate and water in the pH range

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[1] R. K. Murmann, "The Rate of Oxygen Exchange between ReO_4^- and H_2O," Journal of Inorganic Nuclear Chemistry, XVIII (1961), 226.

2.2 to 6.2. He found that the rate of exchange increased rapidly with increasing acidity.

It is well known that chlorine exchanges do take place in compounds of transition elements, so a search of the literature (see next chapter) was made to determine if a chlorine exchange had been shown to occur for the hexachlororhenate ion. Preliminary work done by J. D. Woods[1] at Oak Ridge National Laboratories (1961) indicated that some type of exchange might have taken place, but no thorough analysis was made beyond that point. Jezowska-Trzebiatowska, Nawojska, and Wajda[2] had studied this same reaction in Warsaw, Poland in 1959 and found no exchange.

Numerous experiments have shown that the chlorine-rhenium (IV) does undergo substitution, but very slowly. Noddack and Noddack[3] have shown the $ReCl_6^{-2}$, will undergo at least partial hydrolysis to $ReOHCl_5^{-2}$ and $Re(OH)_2Cl_4^{-2}$,

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[1]Statement made by Joe D. Woods, Associate Professor of Chemistry at Drake University, in a personal interview.

[2]B. Jezowska-Trzebiatowska, J. Nawojska and S. Wajda, "A Study of Fadiochlorine Exchange by Hexachlororhenate (IV)," Bulletin de l'Academie Polonaise des Sciences Cl. III, V, No. 11 (1957), 1081-1084.

[3]Ida Noddack and Walter Noddack, "Sauerstaff--und Halogenverbindungen des Rheniums," Zeitschrift fur anorganishe und Allgemeine Chemie, CCXIV (1933), 161.

and that these complexes reconverted to $ReCl_6^{-2}$ when placed in hydrochloric acid. Due to these seemingly contradictory results, the experiment was performed.

II. DEFINITIONS OF TERMS USED

Background. Background is the radioactivity present in the atmosphere and from which no object can escape.

Beta particle. A large number of radioactive atoms produce beta rays (beta particles) upon disintegration. A beta ray consists of either a positron or an electron produced by nuclear transformations within the decaying atom. Beta rays can vary appreciably in energies, ranging from a few thousand electron volts to several million electron volts. The velocity and penetrating power of a beta ray depends directly on its energy.

Chlorine-36. The element chlorine contains 17 protons in its nucleus, but the radioactive isotope chlorine-36 has in addition, 19 neutrons in its nucleus. This isotope is produced by bombarding the chlorine-35 atom with a "slow neutron" which remains in the nucleus. Since atoms of molecular number or twenty or less are most stable when their neutron-proton ratio is unity, chlorine-36 emits a beta ray to decay to the much more stable argon-36. The

chlorine-36 atom emits a beta particle which has an energy of .66 million electron volts and has a half-life of 3×10^5 years.

Counts per minute. The term counts per minute shall be used to mean the observed counting rate of disintegrations per minute. The rate is directly proportional to the number of radionuclides present. This is the apparent activity as compared to the specific activity (see below).

Exchange reaction. Exchange reaction is a process in which atoms of a given element interchange between two or more different compounds containing that element.

Gas-flow detector. Gas-flow detector is a Geiger-Müeller counter whose ionization chamber is continuously being replenished with gas. The molecules of this gas are ionized when struck by radio-particles. The ionized molecules come into contact with an electrode where it is neutralized and produces an electrical pulse in a circuit. A counting circuit contains meters which measure the pulses and thus the radioactivity.

Half-life. The half-life of any radionuclide is the time necessary for the activity of the atom to decrease by 50 per cent.

Rhenium. Rhenium is transition element number seventy-five and third member of the manganese family. Its natural occurring isotopes are 185 and 187 (beta emitter), its density 20.9 g/cc, melting point 3137 C^{o}, ionization potential (first electron) 7.87 volts, covalent radius 1.278 $\mathring{A}$, and its oxidation states being 7, 4, 6, 5, 2, 3, 1, and -1.

Self-absorption. Self-absorption is a rather self-explanatory word which means the absorption of radioactive particles from a sample by the overlying layers of material of that sample. Self-absorption is particularly significant in alpha and beta analyses since their range in an absorbing medium is low.

Specific activity. Specific activity is the amount of radioactivity per milligram of sample.

Tagged. A molecule which possesses a radioactive atom is said to be a "tagged" molecule. The radioactive atom is called a tracer atom. In this work it is indicated by an asterisk.

CHAPTER II

A SEARCH OF THE LITERATURE

The general equation for an exchange reaction may be written as follows:

$$AZ_6 + BZ^* \dashrightarrow AZ_5Z^* + BZ$$

McKay[1] has shown in his derivation of the first-order rate law of exchange, that the rate of disappearance of the radioactive isotope from the labeled reactant to the unlabeled reactant can be determined. G. M. Harris[2] later showed that this rate law will be applicable irrespective of the reactant concentrations, or the concentration of the labeling isotope. The law will also hold true regardless of the actual mechanism of the exchange, the number of exchangeable groups and differences in isotopic reaction rates providing tracer amounts are used.

Determinations of rates and mechanisms of exchange of transitional elements using the tracer technique can be classed in one of two groups: (1) those using the metal

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[1]H. A. C. McKay, "Kinetics of Exchange Reactions," Nature, CXXXXII (December 3, 1938), 997.

[2]G. M. Harris, "Kinetics of Isotopic Exchange Reactions," Transactions of the Faraday Society, XXXXVII (1951), 716.

as the tagged atom, and (2) those using the tagged ligand. The latter procedure has a number of advantages which make it the preferred method. First, the probability of observing an exchange is considerably less using a tagged metal as compared to its corresponding ligand exchange since several bonds must be broken. Taube[1] has shown that it is possible to have a measurable ligand exchange while its metal counterpart will be immeasurably slow.

Long[2] has observed difficulties in separation of metal exchanges. Often precipitation occurs with the addition of another metal as in his experiment with Ni^{+2*} and $Ni(CN)_4^{-2}$. Little more can be done with the data from such experiments than to compare the rate of the exchange with that of the rate of the precipitation of the salt.

Thirdly, in metal exchanges, oftentimes several intermediate complexes are formed making it difficult to interpret the data collected. Wolfgang and Dodson[3]

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[1]Henry Taube, "Rate and Mechanic of Substitution in Inorganic Complexes in Solution," Chemical Reviews, L (June, 1952), 77.

[2]F. A. Long, "Exchange Reactions of Tetracyanonickelate Ion: The Structure of Nickle Cyanide," Journal of the American Chemical Society, LXXIII (February, 1951), 537.

[3]Richard L. Wolfgang and Richard W. Dodson, "Kinetics of Exchange and Disproportionation Reactions in Mercuric Cyanide Solutions," Journal of the American Chemical Society, LVI (April 5, 1954), 2004.

encountered this difficulty using Hg^{+2*} and $HgCN^{+1}$.

One of the earliest kinetic isotopic exchange studies was performed by Duffield and Calvin.[1] In working with copper chelate compounds in pyridine solution they found that the rate was dependent on the reciprocal of the reactant concentrations, and therefore followed a second-order law. It would seem highly likely that the copper chelate complex becomes substantially modified on solution in pyridine such that a complex with one or two coördinated pyridine ligands are formed. The resultant complex might be more labile to substitution. If such a process were operative, the observed lability would be that of the intermediate solvated complex rather than that of the parent complex.[2] West[3] suggests, from his studies of cobalt complexes of substituted salicylaldehyde bidentates with cobalt acetate in water, that this same mechanism prevails in that reaction.

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[1]R. B. Duffield and M. Calvin, "The Stability of Chelate Compounds. III. Exchange Reactions of Copper Chelate Compounds," Journal of the American Chemical Society, LXVIII (April, 1946), 557.

[2]D. R. Stranks and R. G. Wilkins, "Isotopic Tracers in Inorganic Chemistry," Chemical Reviews, LVII (October, 1957), 785.

[3]B. O. West, "Studies on Bond Type in Certain Cobalt Complex Compounds Part IV. The Exchange Reactions of Quadridentate Complexes," Journal of the Chemical Society of London (1954), 395-400.

Ligand exchange studies have greatly increased in number, as compared to the metal exchanges, with the square complexes of Pt(II) and Au(III) of special importance. Grinberg and Nikolskaya[1] have made a detailed kinetic study of the $(PtBr_4)^{-2}$ and Br^{-1*} system which revealed that the rate is approximately first order in complex concentration but independent of the bromine-ion concentration. This makes it consistent with both the Sn1 and Sn2 aqueous solution mechanisms. However, when the K_2PtBr_4 was allowed to "age" in aqueous solution before being mixed with the labeled potassium bromide solution, the exchange rate increased with the "age" of the solution.[2] This "aging" represents the gradual establishment of the equilibrium concentration of the intermediate aquo complex; mechanism Sn2 is therefore favored.[3]

Grantham, Elleman, and Martin[4] found the same results in the $PtCl_4^{-2}$ and Cl^{-1*} exchange. In both cases

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[1]Stranks and Wilkins, op. cit., p. 788; and A. A. Grinberg and L. E. Nikolskaya, Zhur. Priklad. Khim, XXIV (1951), 893.

[2]Ibid. [3]Ibid.

[4]LeRoy F. Grantham, Thomas X. Elleman, and Don S. Martin, "Exchange of Chlorine in Aqueous Systems Containing Chloride and Tetrachloroplatinate II," Journal of the American Chemical Society, LXXVII (June, 1955), 2965.

the strength of the platinum-halide bond in the intermediate aquo-complex is determined. This cannot be done for the reacting platinum halide since the rate constant in that instance is that of the aquation process.

In most ligand reactions it is found that the mechanism is seldom a direct ligand exchange, but rather the first step is that of aquation. This is especially true in complexes of coördination six. Ruttenberg and Taube[1] demonstrated this in their reaction of $Co(NH_3)_5H_2O^{+++}$ and Cl^{-1}. Their observations indicated that the Sn2 mechanism (shown below) predominated over the Sn1.

$$Co(NH_3)_5H_2O^{+3} \longrightarrow Co(NH_3)_5^{+3} + H_2O$$

$$Co(NH_3)_5^{+3} + Cl^{-1} \longrightarrow Co(NH_3)_5Cl^{+2}$$

Rich and Taube[2,3] have made observations of exchange rate differences due to catalysts in $AuCl_4^{-1*}$ and $PtCl_6^{-1}$

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[1]A. C. Ruttenberg and Henry Taube, "The Exchange of Water between $Co(NH_3)_5H_2O^{+++}$ and Solvent,*" Journal of Chemical Physics, XX (May, 1952), 825.

[2]Ronald L. Rich and Henry Taube, "Induced Exchange of Cl^- and $AuCl_4^-$. Evidence for Au(II)," Journal of Physical Chemistry, LVIII (January, 1954), 6.

[3]Ronald L. Rich and Henry Taube, "Catalysis by Pt(III) of Exchange Reactions of $PtCl_4^{-2}$ and $PtCl_6^{-2}$," Journal of the American Chemical Society, LXXVI (May 20, 1954), 2608.

chlorine reactions. Fe^{+2} enhances the $AuCl_4^{-1*}$ reaction, while Ir^{+4} has an opposite effect on the $PtCl_6^{-1}$ exchange. They have postulated that these variations in rate are due to unusual oxidation states in the intermediate steps of the mechanisms, thus making the central atom much more susceptible to exchange. $PtCl_6^{-1}$ and Cl^{-1*} is extremely photosensitive, and thus Iridium is added to the reaction solution to produce a measurable rate.

Complexes in the VIIB group have shown exchanges in the complexes of coördination number six. Weinland and Lauenstein as early as 1899 showed that a solution of the compound K_2MnF_6 in water hydrolyzes slowly; even in the presence of hydroxide or carbonate ions, the reaction takes place at a measurable rate.[1]

As stated previously on pages 3 and 4, $ReCl_6^{-2}$ is known to hydrolyze to $Re(OH)_2Cl_4^{-2}$, and then reconvert to $ReCl_6^{-2}$ when placed in HCl. Maun and Davidson[2] have demonstrated that the method of preparation has a great influence on the properties of $ReCl_6^{-2}$ in hydrochloric acid.

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[1]Taube, op. cit., p. 105; and R. F. Weinland and O. Laurenstein, "Über Fluormanganite," Zeitschrift für anorganishe und allgemeine Chemie, XX (1899), 40.

[2]Eugene K. Maun and Norman Davidson, "Investigations in the Chemistry of Rhenium. I. Oxidation States IV, V, and VII," Journal of the American Chemical Society, LXXII (May, 1950), 2254.

Rhenium complexes have been shown to exchange in several instances. Murmann[1] observed that ReO_4^- and H_2O will undergo a rapid oxygen exchange in acidic conditions. He mixed finely powdered $NaReO_4^*$ (asterisk denotes O^{18}) with shaking to 10.0 ml of H_2O slightly acidified with HNO_3 at 0° C. Samples were withdrawn at intervals and added to 2M $AgNO_3$ solutions at 0° C. The precipitate ($AgReO_4$) was collected, washed two times with water, three times with methanol, and dried under vacuum. The precipitate was then decomposed at 1000° C to Re_2O_7, Ag°, O_2 and lower oxides of Re. The O_2 was purified by freezing with MeOH-CO_2 mixture and the O^{18}/O^{16} ratio determined with an isotope-ratio mass spectrometer and compared with normal O_2 prepared by the thermal decomposition of BaO_2. The isotopic composition of water was determined by equilibrating with a small amount of $NaReO_4$ after the addition of a trace of acid followed by conversion of ReO_4 to O_2. In comparing the O^{18}/O^{16} ratio of the oxygen from the precipitate to the oxygen in the original $NaReO_4^*$, it was found that the precipitate ratio was much lower. This indicates exchange, for the precipitate ratio was still appreciably higher than the BaO_2 ratio. Likewise, the water ratio proved to be much

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[1]Murmann, op. cit., p. 231.

higher than the BaO_2, thus indicating that it obtained O^{18} when the $NaReO_4$* was in solution.

Murmann[1] also noted that there was an oxygen exchange between $[Re(en)_2O_2]^+$ and H_2O. Using $[Re(en)_2O_2]$ Cl evacuated in a Urey tube, he added H_2O* through the stopcock while freezing. This mixture was allowed to warm to about 5° C. until solution and mixing were complete. About .2g of H_2O was distilled off and collected. A second sample was taken an hour later. The samples were equilibrated with a known amount of CO_2 and the isotopic composition of the CO_2 measured. Although realizing that the experimental error was high, Murmann concludes that the values are in closer agreement with slow exchange.

Although many exchange reactions have been performed, there is still a great deal of data to be collected, especially on the more rare elements such as rhenium. So, with the literature background in this chapter in mind, the research on the exchange of HCl^{36} and K_2ReCl_6 was carried out.

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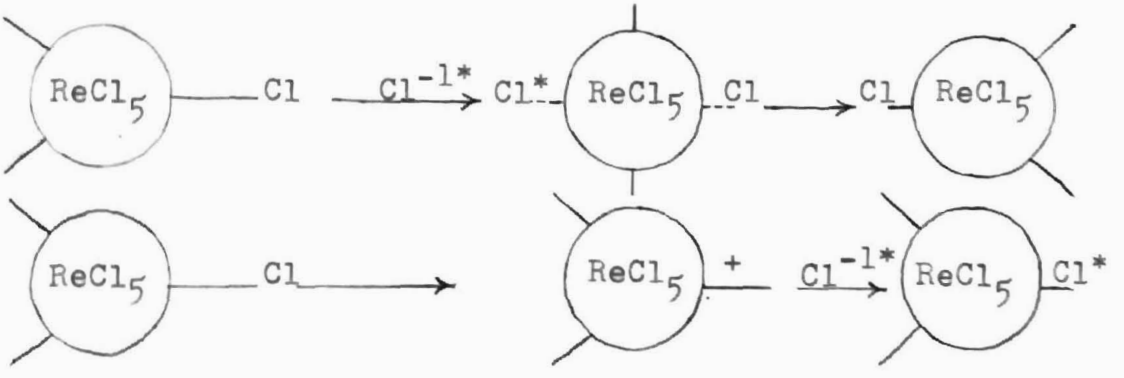
[1] Ibid., p. 232.

CHAPTER III

EXPERIMENTAL TECHNIQUE

It was proposed to determine if there is an exchange of chlorine ions if a hexachlororhenate compound is placed in a hydrochloric acid solution. It was further proposed that if such an exchange actually does take place, the rate of exchange would be determined by allowing the hexachlororhenate to remain in solution for varying lengths of time. Finally, insight into the mechanism of the reaction might be obtained by allowing the exchange to take place for a convenient time limit and keeping all ions except the H-ion at a constant concentration. The diagrams below illustrate two possible mechanisms for an exchange reaction to occur:



In case (1), a tagged chlorine ion, through some activated complex, replaces another chlorine directly. In case (2),

ionization first occurs followed by a reaction of the positive ion with a tagged chlorine-ion from solution. If a dependency of reaction rate on pH values was found, one might expect competition between Cl^{-1*} and hydroxide ions in reacting with the positive complex ion.

I. PRELIMINARY WORK

Materials and apparatus. The materials used in experimentation consisted primarily of pipettes, beakers, glass sintered filters, a four-place analytical balance, and planchets. The only apparatus which needed preliminary calibration was the gas flow detector. The instrument used was Nuclear-Chicago's model D-47 gas flow Geiger-Müller counter.

Radioactive counting technique. Although the counter can be used as a proportional windowless counter as well as a Geiger counter, a number of preliminary samples were counted by both methods, and the proportional arrangement showed no greater counting efficiency. The actual efficiency of the counter was determined by taking several fifteen minute counts of a known 10,000 counts per minute Carbon-14 sample. It was determined to be 88 per cent efficient.

Because of the structural limitations imposed by the restrictions of the electrostatic fields in high-voltage

counters and because of the limitations imposed by the electronics that are necessary to record counts on a mechanical register, there is a voltage minimum below which most proportional and Geiger counters will not operate.[1] This minimum voltage is called the threshold voltage, and it varies with the type of instrument used. The first step in the determination of the operating potential is to obtain the threshold. Using again the known Carbon-14 sample and taking five minute counting periods, the voltage is slowly raised until this threshold is reached. Once this point is obtained, the counting rate will level off with increasing voltage. This level in the counting rate may last for several hundred volts before another abrupt increase in rate is reached. At this point the counter is in a "continuous" discharge. The operating potential chosen is located on this plateau about 100 volts higher than threshold. The advantage of using a potential on the plateau is that the sensitivity of the counter is not greatly affected by small changes in the high voltage. Figure 1 shows the plateau curve determined for this research. From this curve, 1200 volts was selected as the operating potential to be used in the remainder of the procedures.

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[1]Ralph T. Overman and Herbert M. Clark, Radioisotope Techniques (New York: McGraw-Hill Book Company, Inc., 1960), p. 51.

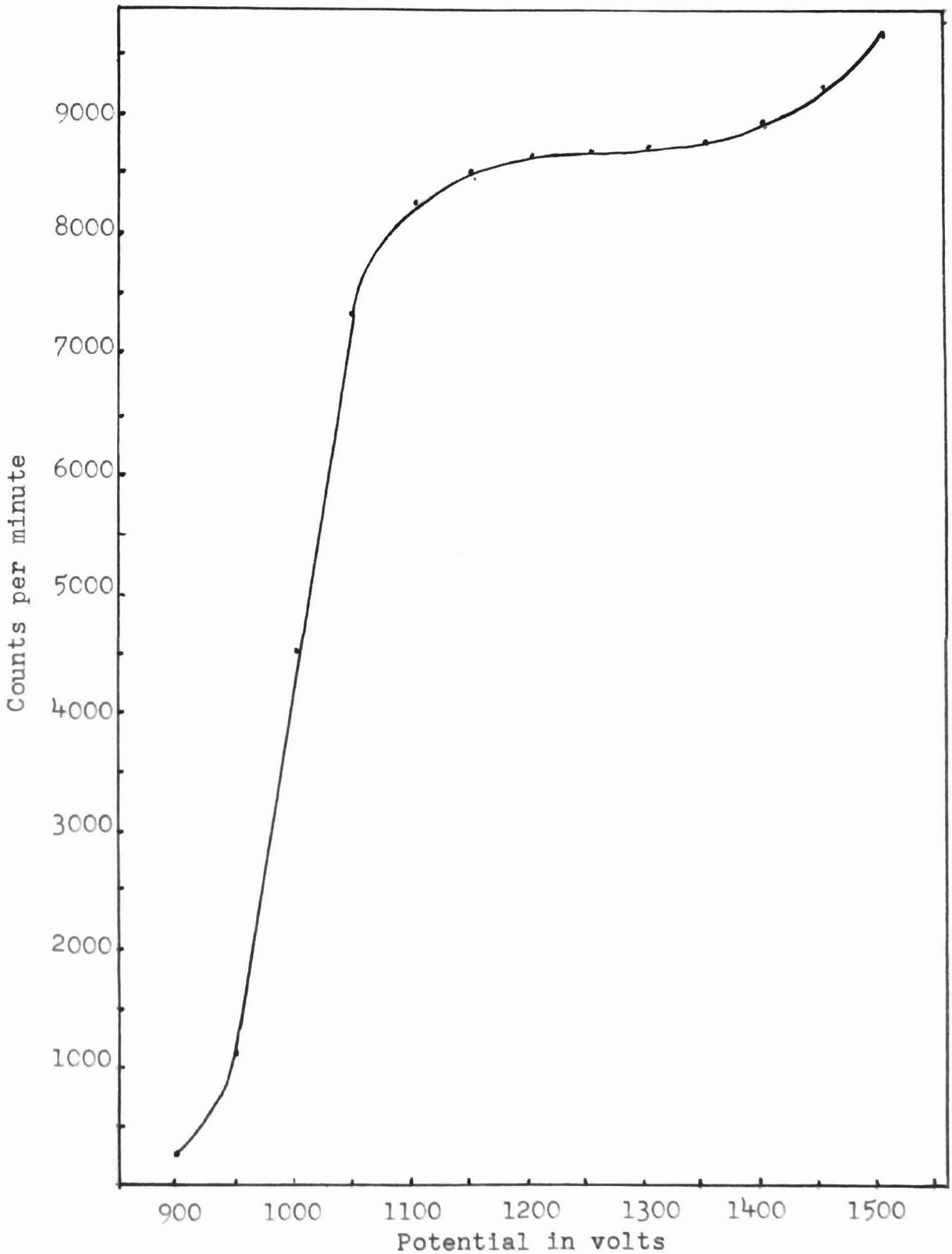

Figure 1. Operating potential.

Preparation of chemicals as reagents. Two stock solutions were prepared to be used in sample analysis and the collection of data. The first was K_2ReCl_6, prepared by the procedure outlined in Volume I of Inorganic Synthesis.[1] One and one-half grams of commercial K_2ReO_4 was mixed with 3 grams of KI powder. The mixture was placed in a covered beaker and heated with 50 milliliters of HCl until most of the iodine was condensed on the cover. The solution was then heated for an additional 30 minutes just below the boiling point and with the beaker cover removed. Finally the solution was allowed to evaporate to dryness.

The residue was dissolved in 30 ml of 10 per cent HCl and again heated to just below the boiling point for 10 minutes. The solution was then cooled in an ice bath for 6 hours, and the brownish-yellow precipitate filtered and washed with cold 10 per cent HCl on a sintered-glass filter.

This impure product was digested in 100 ml of HCl (Sp. Gr. 1.2) until the solution was a bright green color. This solution was then evaporated to 25 ml and cooled

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[1] L. F. Audrieth, J. C. Bailar, Jr., W. C. Fernelius, W. C. Johnson, and R. E. Kirk, Inorganic Synthesis (New York: McGraw-Hill Book Company, Inc., 1939), I, 178. (Submitted by Loren C. Hurd and Victor A. Reinders.)

slowly to 20° C. Finally it was cooled in an ice bath, filtered and washed with 5 ml portions of cold 10 per cent HCl, ethyl alcohol, and diethyl ether. The equation for the reaction is as follows:

$$2KReO_4 + 16HCl + 6KI \text{ ---- } 2K_2ReCl_6 + 4KCl + 8H_2O + 3I_2$$

The second stock solution prepared was that of Nitron acetate, which was used as a precipitant. This solution was used by Geilmann and Voigt[1] in their work with the perrhenate ion (ReO_4^{-1}). Eight grams of nitron ($C_{20}H_{16}N_4$) was dissolved in 3 ml of glacial acetic acid. This was then diluted to 100 ml with distilled water. A few sample analyses showed this solution to be quantitatively acceptable as a precipitant of the hexachlororhenate ion.

II. EXPERIMENTAL PROCEDURE

The experiments were then carried out in the following manner.

1. The K_2ReCl_6 samples were weighed out in a 50 milliliter beaker to the tenth of a milligram. The weighing was done by difference, and the weights kept within a three to five milligram range in most instances.

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[1]Von W. Geilmann and A. Voigt, "Die Bestimmung löslicher Perrhenate mit Hilfe von Nitron," Zeitschrift für anorganische und allgemeine Chemie, CLXXXXIII (1930), 312.

2. One milliliter of hydrochloric acid was added to the beaker, and the mixture allowed to stand until the entire sample had dissolved.
3. To this solution one hundred lambda of radioactive chlorine was added. The chlorine-36 was in a solution as potassium chloride, and had been calibrated for its activity. It was assumed that the addition of the common potassium ion to the reacting solution would not affect any quantitative exchange which might take place.
4. The exchange solution was then heated slowly to 80° C. Geilmann and Voigt[1] had used this step in their experiments, but also proved it to be unnecessary. Later sample analysis supported their belief, and thus the heating process was eliminated.
5. After the reaction was allowed to stand for a predetermined length of time, the hexachlororhenate-nitron complex was precipitated from solution with the nitron acetate solution. During the precipitation the solution was cooled in an ice bath. This cooling was also later eliminated from the procedure.

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[1] Ibid., p. 314.

6. Once precipitation was complete, the solution was filtered on a sintered glass filter.
7. The precipitate was washed with two one-milliliter portions of 10 per cent hydrochloric acid, and this followed by ethanol and diethyl ether washings of the same number and magnitude. The filtrate and the washings were caught in a ten milliliter volumetric flask and saved for further analysis.
8. The precipitate was then dried under a one hundred watt infra-red lamp for fifteen minutes. This length of time proved to be sufficient for thorough drying.
9. A planchet was weighed to the tenth of a milligram.
10. The precipitate was removed from the filter and placed on the weighed planchet.
11. The precipitate was placed in a lead shielded gas-flow Geiger tube, and the radioactivity counted for a fifteen minute interval.
12. The planchet and precipitate were now weighed to verify the accuracy of the quantitative technique.
13. Next the filtrate and washing were analyzed. The solution was neutralized with sodium bicarbonate.

14. Enough distilled water was added to bring the volume of ten milliliters.
15. One hundred lambda of the neutralized solution was placed on a planchet and placed under the infra-red lamp. It was allowed to evaporate to dryness.
16. The evaporated sample was then placed in the gas-flow chamber and counted. In this way all beginning activity can be taken into account.
17. Two samples of potassium perrhenate were placed in a radioactive acid solution, and the above precipitation procedures were repeated. This was to determine the efficiency of the washing procedure in its effort to eliminate all radioactive solution which may have been adhering to the precipitate.
18. Finally, data for an absorption curve had to be collected and a curve constructed to determine if the crystals remaining after filtrate evaporation were self-absorbing activity. This was done by taking several different aliquots of filtrate and counting their activity. This activity was then compared to the specific activity of the sample. An absorption curve was also constructed for the precipitate and for the Chlorine-36 activity samples.

The data collected in the above-mentioned procedures, and any relationships or trends are discussed and analyzed by graphical and tabular form in the succeeding chapters.

CHAPTER IV

COLLECTION AND ANALYSIS OF DATA

I. PRELIMINARY EXPERIMENTS

Precipitating procedure. In order to validate the method used to determine the chlorine exchange from hydrochloric acid to potassium hexachlororhenate, an initial series of tests were conducted to determine the analytical precision, reproducibility, and accuracy of the precipitation used in the collection of the data for this thesis. Several reagents were considered as possible precipitants. Willard and Smith[1] have used tetraphenylarsonium chloride to precipitate perrhenate, while Geilmann and Voigt[2] did the same with nitron. Another possibility is trioctylamine hydrochloride dissolved in cyclohexane which Boyd[3] has used to precipitate K_2ReCl_6.

Two series of tests were run, with five samples in

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[1]Hobart H. Willard and George M. Smith, "Tetraphenylarsonium Chloride as an Analytical Reagent," Industrial and Engineering Chemistry-Analytical Edition, XI (1939), 305.

[2]Geilmann and Voigt, op. cit.

[3]G. E. Boyd, "Technetium and Promethium," Journal of Chemical Education, XXXVI (January, 1959), 10.

each series. In the first set of precipitations, solutions of K_2ReCl_6 and HCl were prepared according to the procedure on pages 20 and 21. The samples of K_2ReCl_6 were placed in one milliliter of 2N HCl and allowed to dissolve. After the samples were completely in solution, the solutions were heated to 80° C. for twenty minutes before 100 lambda of nitron acetate was added. The solutions were allowed to cool slowly to about room temperature, and then placed in an ice bath to cool it further. After precipitation was complete, the precipitates were filtered and washed with more nitron acetate, 10 per cent HCl and ethyl ether. After the washings the precipitates were dried under the heat lamp and weighed.

In the second set of tests, several steps in the above procedure were omitted in an effort to determine what procedures could be shortened. In these tests three procedures were eliminated: (1) heating the solution to 80° C., (2) cooling the solution in an ice bath, and (3) washing the precipitate with more nitron acetate. The results of these two preliminary tests are given in Tables I and II.

TABLE I

AN ANALYTICAL EVALUATION OF NITRON ACETATE AS A PRECIPITANT

Weight of K_2ReCl_6	Weight of Precipitate	Expected Weight of Precipitate	Per Cent Difference
.0048 g	.0074 g	.0078 g	5.3
.0034	.0052	.0056	7.1
.0037	.0058	.0061	4.8
.0051	.0080	.0084	5.0
.0041	.0064	.0068	5.9

From Table I it is evident that nitron acetate will precipitate the hexachlororhenate complex analytically. The margin of error in weight loss is less than 7.1 per cent, or .4 mg in every case. Since the error in radiation counting is 5 to 10 per cent itself, this weight loss is within the expected experimental accuracy.

TABLE II

AN ANALYTICAL EVALUATION OF NITRON ACETATE AS A PRECIPITANT*

Weight of K_2ReCl_6	Weight of Precipitate	Expected Weight of Precipitate	Per Cent Difference
.0052 g	.0082	.0086	4.7
.0046	.0074	.0076	2.7
.0033	.0052	.0055	5.5
.0039	.0061	.0065	6.2
.0041	.0066	.0068	2.9

*Using the abbreviated procedure

The results in Table II, while adding more support to the acceptability of nitron acetate as a precipitant, also goes one step further. Table II shows that omitting the three procedures listed above does not affect the precision and accuracy of precipitation. In fact, the magnitude of error is less in the second tests than in the first, for only one of the five samples in Table I has less than a 5 per cent difference; while in Table II, three of the samples have less than 5 per cent differences. This confirms Geilmann and Voigt's[1] work, for they found that eliminating the heating process did not affect the precipitation. These three steps were omitted during the remainder of the experiment.

Tagging procedure. With this part of the preliminary work completed, the next series of measurements were made to determine the amount of radioactive chlorine necessary for tagging the hydrochloric acid solution to be used in the exchange experiments. The chlorine to be used was obtained from the Atomic Corporation in Panorama City, California. Since this was in salt form (KCl^{36}), danger from gaseous fumes was negligible. It was decided to place enough radioactivity in the solution so that the exchange system would have at least 20,000 disintegrations per minute.

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[1]Geilmann and Voigt, loc. cit.

Before this could be accomplished it was necessary to determine how "hot" the source was. Ten lambda of the active KCl was placed on a planchet and evaporated to dryness under the heat lamp. The dried salt was then placed in the counting chamber of the Geiger-Müller counter for a ten minute counting period. Larger volumes of the source were also counted to determine if self-absorption was taking place in the dried salt. Table III below gives the results obtained from these counts.

TABLE III

DETERMINATION OF RADIOACTIVITY IN SOURCE

Sample Volume	Time	Recorded Activity	Activity in Counts/Minutes	Project, to 100 λ
10 λ	10 min.	26,237 c/m	2,624 c/m	26,237
10	10	26,235	2,624	26,235
10	10	25,886	2,589	25,886
10	10	26,044	2,604	26,044
10	10	25,942	2,594	25,942
20	10	52,372	5,237	26,185
20	10	52,404	5,240	26,202
25	10	65,024	6,502	26,010
50	10	129,839	12,984	25,968
50	10	129,992	12,999	25,998

The results in column 4 of Table III (the activity of the sample in counts per minute) were plotted against the volumes in column 1. The resulting Absorption Curve is

shown in Figure 2. The average of the activity at any given volume was used as the amount of activity at that volume. Since the plot is a straight line, it is concluded that self-absorption is not taking place. If self-absorption were a factor, then the activity of the larger samples would not increase proportionately with the increase in volume. The graph would instead be a line that would curve until it was horizontal to the volume axis (x-axis).

Since self-absorption is not taking place, the sample activity values were projected to a 100 lambda volume. These projected activities listed in column 5 of Table III were averaged to determine the activity in 100 lambda of the source material. This value of 26,070 counts per minute was the one used as the activity of 100 lambda.

II. ISOTOPIC EXCHANGE EXPERIMENT

The next experiment carried out was to determine if there is an exchange of chlorines between a 2N HCl solution and K_2ReCl_6. In this experiment the reaction time was varied from sample to sample. The length of times ranged from 30 minutes to 2 weeks. Three samples were taken at each interval, and the method of preparation and reaction was performed according to the experimental procedure described in Chapter III, pages 20 and 21. The results of these determinations are given in Table IV, page 32.

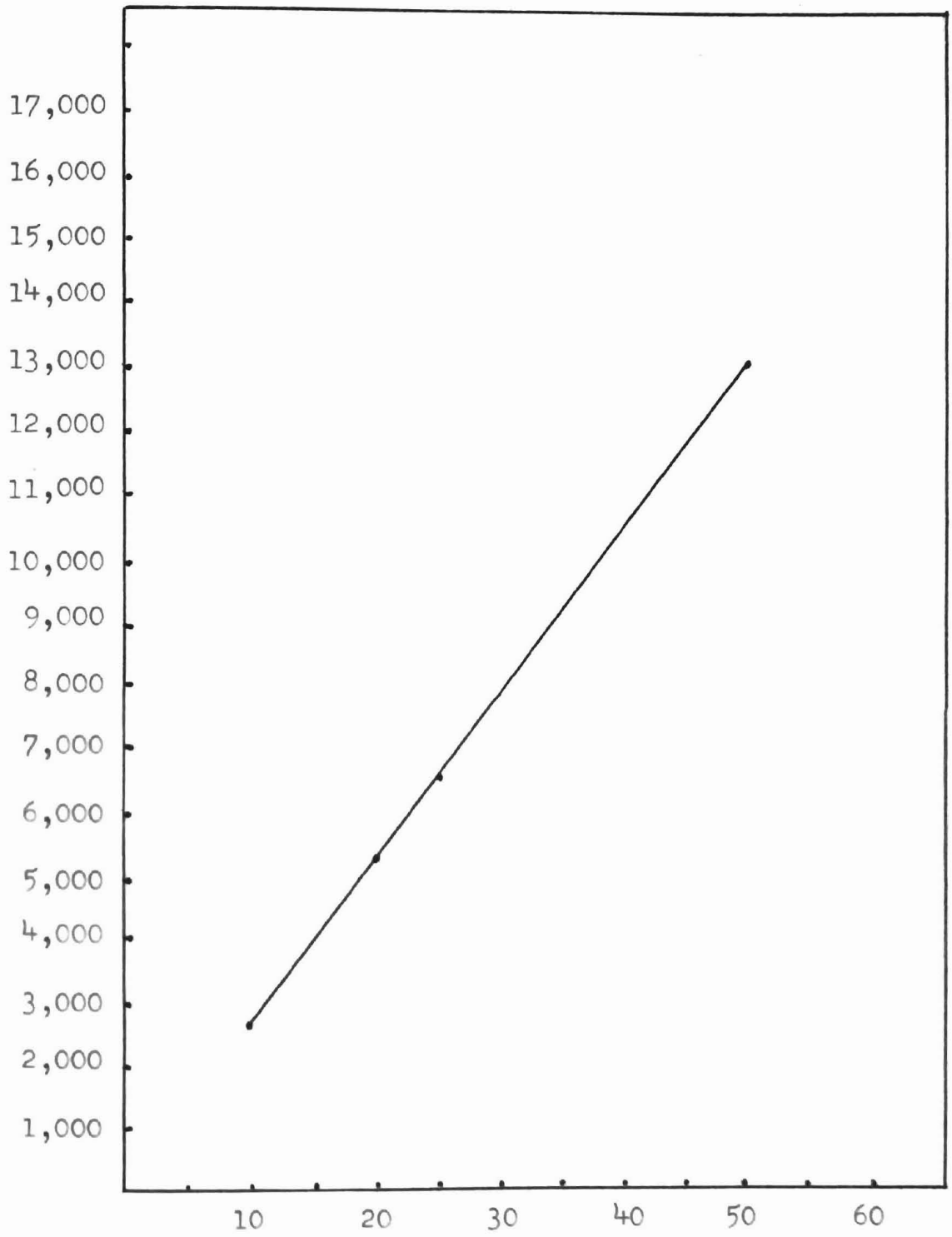

Figure 2. Self-absorption in radioactive source.

TABLE IV

DETERMINATION OF CHLORINE EXCHANGE BETWEEN Cl^- AND $(ReCl_6)^=$ IONS IN A 2N HYDROCHLORIC ACID SOLUTION

Sample Number	Reaction Time	Background Radiation	Activity Counted	Activity in Precipitate
	Minutes			
1	30	38 c/m	150 c/m	112 c/m
2	30	36	115	79
3	30	36	122	86
4	60	30	117	87
5	60	30	131	101
6	60	24	120	96
7	120	24	109	85
8	120	17	106	89
9	120	16	114	98
	Hours			
10	6	27	132	105
11	6	26	124	98
12	6	22	114	92
13	24	22	109	87
14	24	22	118	96
15	24	22	111	89
16	48	22	128	106
17	48	22	116	94
18	48	37	131	94
	Weeks			
19	1	36	122	86
20	1	37	118	81
21	1	38	144	106
22	2	31	125	94
23	2	23	107	84
24	2	15	103	88

Column 3 in Table IV is the background radiation present in the laboratory, which was detected by the counter. Although each sample was counted for a ten minute interval, the activity is expressed in Column 4 as counts per minute. The activity in, or adhering to, the precipitate listed in the fifth column is obtained by taking the difference between Column 4 and Column 3.

The activities in the precipitates from the three samples at the given time intervals were averaged, and these average activities were plotted against the time intervals given in Column 2, Table IV. The resulting graph is shown in Figure 3. (Because the range of the time units is so great, the first two time intervals are not plotted.)

In an effort to insure analytical accuracy, the precipitates were weighed after counting. These weights were compared to the weights which are theoretically possible to obtain in precipitation. Table V gives the comparisons of weights and theoretical values and the per cent of error for each sample. In every case, the error due to loss of material is less than 7.2 per cent. These comparisons and percentages indicate that the procedure is analytically sound.

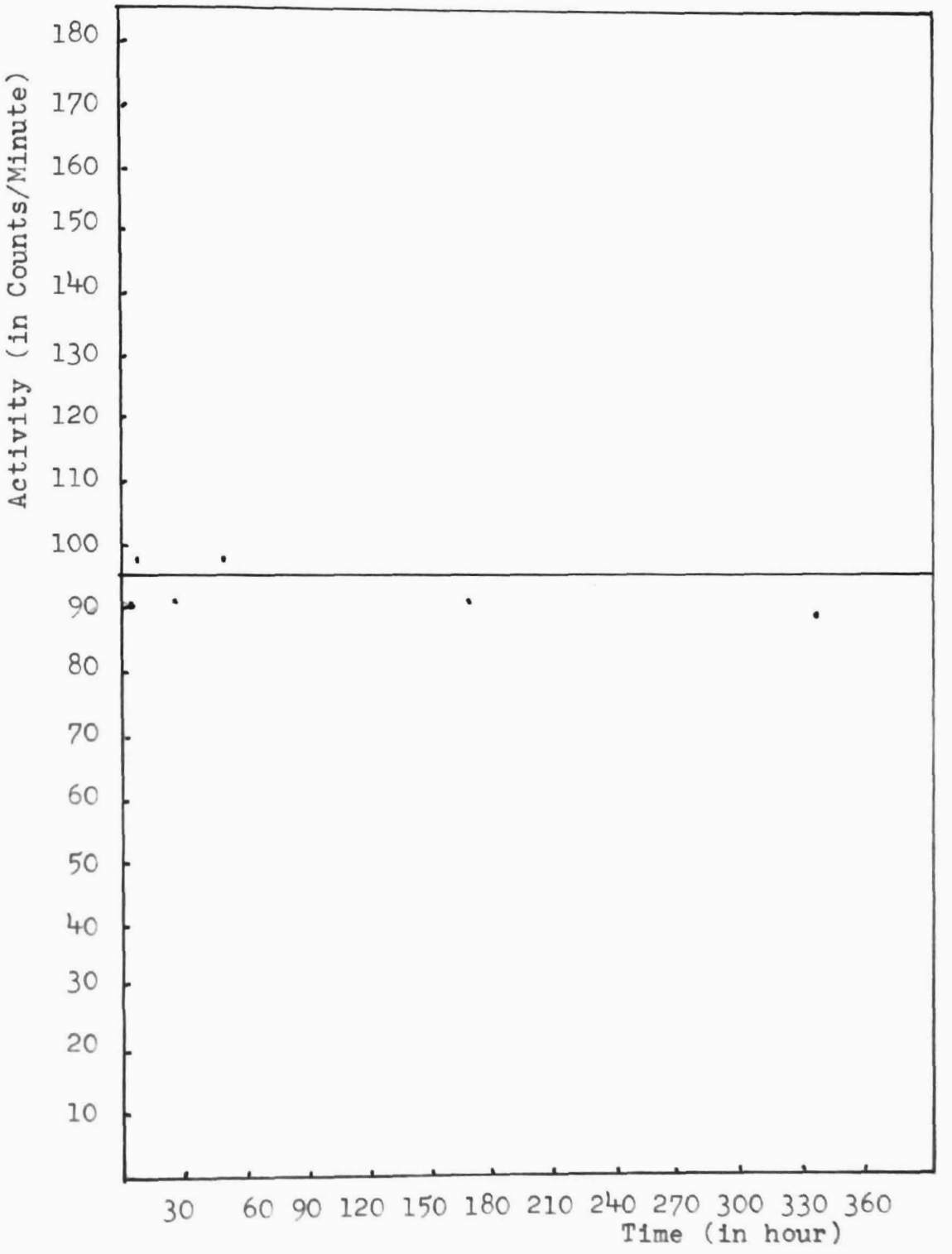

Figure 3. Activity in the precipitate as a function of time. (Nitron-hexachlororhenate)

TABLE V

ANALYTICAL EVALUATION OF THE EXCHANGE EXPERIMENT

Sample Number	Sample Weight	Proportionate Weight	Theory Weight Expected	Weight Losses	Per Cent Loss
1	4.6 mg	7.2 mg	7.6 mg	.4 mg	5.1
2	4.6	7.3	7.6	.3	3.9
3	5.1	8.1	8.4	.3	3.6
4	4.0	6.4	6.6	.2	3.0
5	5.8	9.2	9.6	.4	4.2
6	5.0	8.0	8.3	.3	3.6
7	3.8	5.9	6.3	.4	6.4
8	4.1	6.6	6.8	.2	3.0
9	3.3	5.3	5.5	.2	3.6
10	4.7	7.4	7.8	.4	5.1
11	3.7	5.9	6.1	.2	3.3
12	3.1	4.8	5.1	.3	5.9
13	5.0	8.1	8.3	.2	2.4
14	3.9	6.1	6.5	.4	6.2
15	3.6	5.9	6.0	.1	1.7
16	4.6	7.2	7.6	.4	5.3
17	4.1	6.5	6.8	.3	4.4
18	3.9	6.2	6.5	.3	4.6
19	3.3	5.1	5.5	.4	7.2
20	3.4	5.4	5.6	.2	3.5
21	4.5	7.0	7.4	.4	5.4
22	5.3	8.4	8.8	.4	4.6
23	4.3	6.8	7.1	.3	4.2
24	3.5	5.5	5.8	.3	5.2

Since Table V shows that the procedure in the exchange experiment is analytically acceptable, and since the object of this thesis is to determine if a chlorine exchange does take place between HCl and K_2ReCl_6, the activity in the precipitate must be explained. There are

three possible conclusions to be drawn from the results in Table V.

1. The precipitates do contain some radioactivity, so it is possible that there has been a slow exchange of chlorine atoms between the HCl and K_2ReCl_6.
2. Figure 3 seems to indicate that the amount of activity in the precipitate does not increase with time. This may be due to self-absorption in the precipitate, (and in actuality, the activity in the precipitate may be higher than measured).
3. The radioactivity in the precipitate may be due to mechanical contamination only, and may not have resulted from a chemical exchange reaction.

With these three possible explanations of the results of the exchange reaction data, further experiments were performed in order to determine which, if any, were correct.

III. POST-EXCHANGE EXPERIMENTS

Filtrate activity. As part of the procedure of the exchange experiment, described on page 22 in Chapter III, every sample precipitate was filtered from solution and washed with 10 per cent HCl and diethyl ether. The filtrate and washings from the samples were collected in

a volumetric flask.

Every sample exchange system originally contained 100 lambda, or 26,070 c/m, of radioactive chlorine; so theoretically, the activity in the precipitate and the activity in the filtrate and washings should contain the same total amount. Therefore, the filtrate and washings were then checked for radioactivity. This was done by first neutralizing the solution with sodium bicarbonate, and then adding enough distilled water to bring the volume to 10 milliliters. Next, a 100 lambda aliquot was taken from the solution and dried on a planchet under a heat lamp. The dried salt was then counted for a ten minute period. The results of the counting are given in Tables VI and VII.

In Table VI, the activities of the 100 lambda samples of solution are given in the second column as one minute counts. The actual activities in the 100 lambda samples (c/m - B.G.) are given in Column 4. Since 100 lambda is equivalent to one-tenth of a milliliter, the activity in that volume is only one- one hundredth (1/100) of the total activity in the ten milliliters of filtrate and washing. The values in Column 4 are multiplied by 100 to obtain the total activity in the solution given in Column 5. These values ranged from 23,100 to 25,900 counts.

TABLE VI

DETERMINATION OF THE ACTIVITY REMAINING IN THE SOLUTION

Sample Number	Radiation Counted	Background Radiation	Activity in 100λ sample	Activity Still in Solution
1	283 c/m	24 c/m	259 c/m	25,900 cm/
2	267	24	243	24,300
3	271	24	247	24,700
4	258	24	234	23,400
5	270	24	246	24,600
6	259	24	235	23,500
7	265	24	241	24,100
8	282	24	258	25,800
9	255	24	231	23,100
10	264	24	240	24,000
11	258	24	234	23,400
12	265	24	241	24,100
13	256	24	232	23,200
14	277	24	253	25,300
15	263	24	239	23,900
16	259	24	235	23,500
17	264	24	240	24,000
18	274	24	250	25,000
19	268	24	244	24,400
20	260	24	236	23,600
21	260	24	236	23,600
22	261	24	237	23,700
23	275	24	251	25,100
24	261	24	237	23,700

TABLE VII

ACTIVITY AT THE END OF THE EXCHANGE REACTION

Sample Number	Activity in Solution and Washings	Activity in Precipitate	Total Exchange Activity at the Experiment's End
1	25,900 c/m	112 c/m	26,012 c/m
2	24,300	79	24,379
3	24,700	86	24,786
4	23,400	87	23,487
5	24,600	101	24,701
6	23,500	96	23,596
7	24,100	85	24,185
8	25,800	89	25,889
9	23,100	98	23,198
10	24,000	105	24,105
11	23,400	98	23,498
12	24,100	92	24,192
13	23,200	87	23,287
14	25,300	96	25,396
15	23,900	89	23,989
16	23,500	106	23,606
17	24,000	94	24,094
18	25,000	94	25,094
19	24,400	86	24,486
20	23,600	81	23,681
21	23,600	106	23,706
22	23,700	94	23,794
23	25,100	84	25,184
24	23,700	88	23,788

Table VII shows the tabulation of radioactivity at the end of the exchange reaction. Column 2 is a reproduction of the activity in the filtrate solution, while Column 3 is the activity in the precipitates. These two columns are added to obtain the total radiation at the completion of the reaction. Sample 9 has the smallest total and therefore the largest error. Since only 23,198 c/m are accounted for in this sample, there are 2872 c/m which are not accounted for. This is an 11.6 per cent loss. All the activity of the remaining twenty-three samples, however, were accounted for within 10 per cent.

One explanation of this loss is that there may be self-absorption in counting the dried filtrate salt. In order to determine if this was the case, another short experiment had to be carried out before any final conclusions could be drawn from the data in Table VII.

The filtrate from sample 1 was used, and a number of different aliquots were taken and dried on a planchet. The dried salts from the aliquots were counted and the results of these counts are shown in Table VIII. Another self-absorption curve was constructed by plotting the volume of the aliquots against the activity. This curve is given in Figure 4.

TABLE VIII

SELF-ABSORPTION DATA FOR FILTRATE SOLUTION

Sample Volume	Activity Counted	Background Radiation	Sample Activity
10	60 c/m	30 c/m	30 c/m
30	92	30	62
50	120	30	90
70	150	30	120
100	192	30	162
120	225	30	195
150	273	30	243

The graph in Figure 4 is a straight line, so it can be concluded that self-absorption is not a factor in determining the activity in the filtrate and washings solution.

Since self-absorption is not taking place in the solutions, then there are two possible reasons why the total activity at the completion of the exchange reaction (note last column of Table VII) is as much as 3000 counts less than the beginning activity:

1. A rather large amount of self-absorption is taking place in the precipitates, or
2. The activity was lost in the mechanical manipulations of the procedure.

With these two possible explanations in mind, further experiments were performed to determine which, if either, of these explanations is correct.

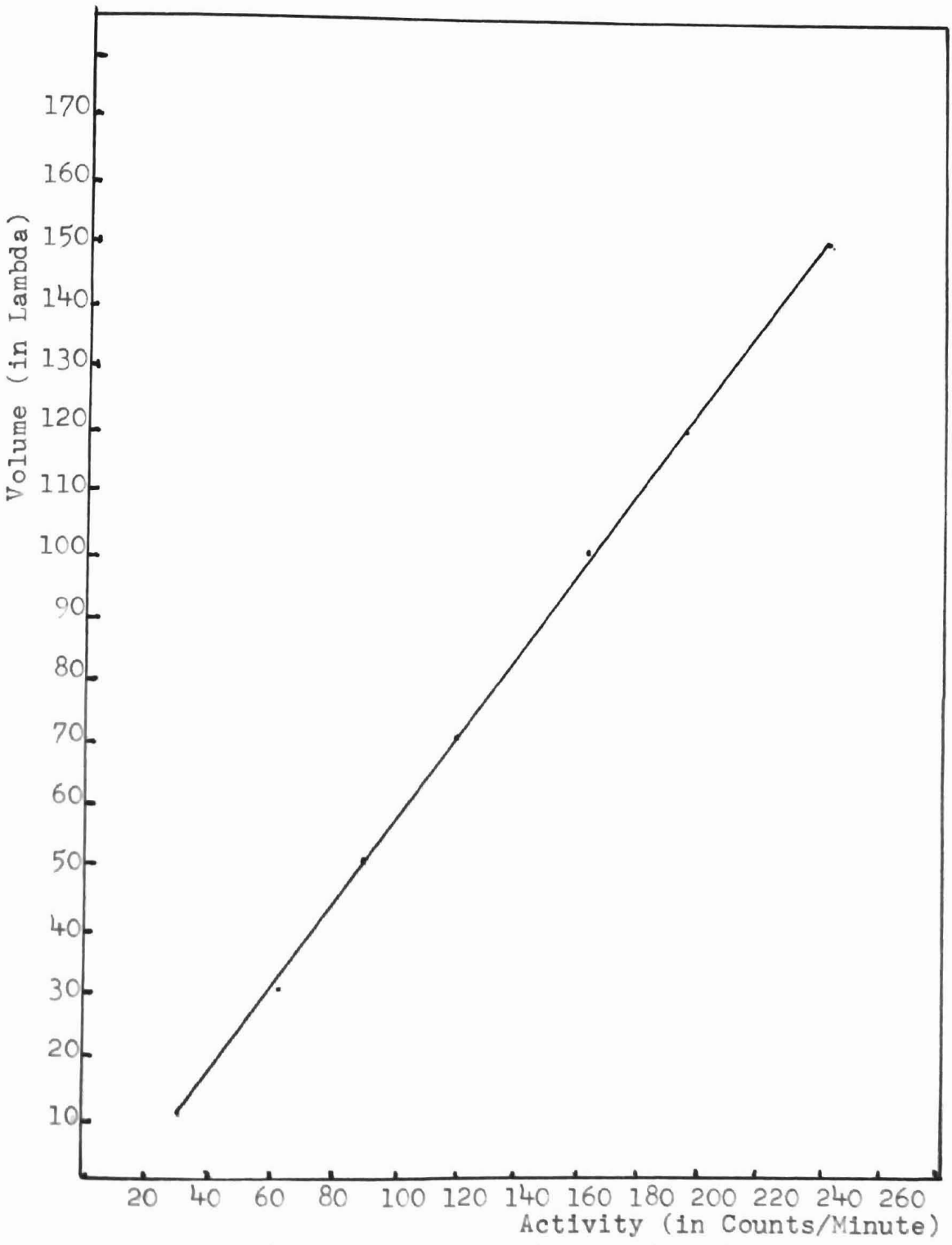

Figure 4. Activity in the precipitate as a function of time. (Nitron-perrhenate)

Perrhenate activity. In this phase of experimentation, potassium perrhenate ($KReO_4$) was carried through the same procedure that the K_2ReCl_6 was in the exchange reaction. It is known that the oxygens in $KReO_4$ will not be substituted by chlorines if placed in an HCl solution. This being true, then, after the perrhenate is precipitated from solution by nitron, all the radioactivity should remain in the filtrate and washings, and none but adhering contamination should be in the precipitate. Table IX gives the results of this trial. It can be noted that at least 74 c/m of activity remained in the precipitate, even though no exchange is possible in this system.

TABLE IX

LOCATION OF RADIOACTIVITY AFTER PERRHENATE PRECIPITATED FROM SOLUTION

Sample Weight	Activity in Precipitate	Activity in Filtrate	Total Activity Accounted for
4.2 mg	80 c/m	24,600 c/m	24,680 c/m
3.6	74	25,100	25,174
3.2	78	24,900	24,978
4.8	85	25,700	25,785
5.4	83	24,100	24,183

With the results in Table IX coupled with the data from previous tables, the validity of some of the possible conclusions to be drawn from the exchange reaction can now

be much more easily determined.

1. The activity found in the perrhenate precipitate in Table IX must be contamination since no exchange is possible. The amount of this contamination is only slightly less than the activity observed in the hexachlororhenate precipitate in Table IV. This suggests that the majority of the activity in the hexachlororhenate precipitate is likewise due to contamination. This is made even more evident by Figure 3 which shows that the amount of activity is not a function of reacting time. These comparisons indicate that no chlorine exchange has taken place between the HCl solution and the K_2ReCl_6.
2. The fact that the activity found in the perrhenate is only slightly less than that in the hexachlororhenate precipitate also indicates that self-absorption is not taking place in the hexachlororhenate precipitate. This also means no chlorine exchange has taken place.
3. From Table IX, the amount of activity observed in the filtrate and washings is also within the range of the activity found in the filtrate and washings of the hexachlororhenate samples in Table VII. Since self-absorption is not a factor

in the precipitate or filtrate solutions in either case, this seems to indicate that out of the 26,070 counts, the 3000 for which there is no account at completion were lost in the mechanics of the procedure. This then leads to the conclusion that all of the radiation not lost in route is in the filtrate. Further, this means again that no chlorine exchange could have taken place between HCl and K_2ReCl_6.

With the above three comparisons of data as indicators that (1) no self-absorption took place in the nitron hexachlororhenate precipitate, (2) no self-absorption took place in the counting of the filtrate activity, (3) that some activity was lost in the mechanical manipulations of the procedure, and (4) that the activity in the nitron-hexachlororhenate was contamination, only one conclusion seems to be evident, and that is: when potassium hexachlororhenate is dissolved in a hydrochloric acid solution, no exchange of chlorines takes place between the two.

CHAPTER V

SUMMARY AND DISCUSSION

A study was made to determine if a chlorine exchange occurs when K_2ReCl_6 is placed in an HCl solution. It was further proposed to determine the rate of the exchange, if one did occur, and to suggest some possibilities as to the mechanism of the exchange.

Experiments to find a suitable precipitant and to determine the activity of the chlorine-36 source had to be performed prior to the main experiment. Finding the precipitant proved to be the more difficult task. Only one solvent extraction method was used on K_2ReCl_6. Since there were several reagents known to precipitate other than rhenium compounds, these were tried on the hexachlororhenate. As it turned out, the first one attempted, nitron, proved to be quantitatively acceptable.

In determining the activity of the source, the possibility of self-absorption had to be checked. This was done by taking larger and larger volumes of the source and measuring their activities. Since activity did increase proportionately with the volume increase, self-absorption was eliminated as a factor. The activity of the source was 26,070 counts per minute for a 100 lambda volume.

Data for the main-body experiment were collected at differing time intervals. These varied from thirty minutes to two weeks in length. Several things made interpretation of the data difficult at first. Radiation was detected in the nitron-hexachlororhenate precipitate, and even a larger amount was missing from the filtrate. Of the total radiation originally in the system (26,070 c/m), as much as 3000 c/m were unaccountable at the conclusion of the experimental samples. Also, as much as 112 c/m were detected in the precipitate. Further experiments had to be performed to determine the significance of the exchange data.

Samples of potassium perrhenate ($KReO_4$) were carried through the same procedure used for K_2ReCl_6. It is a known fact that the chlorine in the HCl will not substitute the oxygens in the perrhenate, and thus, all the activity originally placed in the system should be in the filtrate at the completion. A check of the nitron-perrhenate precipitate showed it to contain only slightly less radiation than the nitron-hexachlororhenate precipitate. This indicated mechanical contamination in both cases.

A test run on the perrhenate filtrate solution showed the same amount of activity present as in the hexachlororhenate filtrate. A self-absorption curve was made for both sets of filtrates. Again, self-absorption was not occurring.

The data from these supporting experiments indicate that in the main exchange experiment (1) the activity in the precipitate is mechanical contamination, (2) that the activity for which there is no account at completion was lost in the manipulations of the procedure.

From these data then, it was concluded that a chlorine exchange does not take place in an HCl - K_2ReCl_6 system, and therefore, the determination of a rate and mechanism of exchange was rendered unnecessary.

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